

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10G 45/62, C07C 5/27	A1	(11) International Publication Number: WO 96/18705 (43) International Publication Date: 20 June 1996 (20.06.96)
(21) International Application Number: PCT/EP95/04997 (22) International Filing Date: 12 December 1995 (12.12.95) (30) Priority Data: 94203628.6 13 December 1994 (13.12.94) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except CA US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400-4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): BLOMSMA, Erwin [NL/BE]; Kardinaal Mercierlaan 92, B-3001 Heverlee (BE). JACOBS, Pierre, August [BE/BE]; Kardinaal Mercierlaan 92, B-3001 Heverlee (BE). MARTENS, Johan, Adriaan [BE/BE]; Kardinaal Mercierlaan 92, B-3001 Heverlee (BE). REINALDA, Donald [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE ISOMERISATION OF A HYDROCARBONACEOUS FEEDSTOCK (57) Abstract Process for isomerisation of a hydrocarbonaceous feedstock substantially boiling in the gasoline range which feedstock comprises linear paraffins having at least five carbon atoms wherein the feedstock is contacted in the presence of hydrogen at elevated temperature and pressure with a catalyst comprising in combination platinum (Pt) and palladium (Pd) each in metallic form supported on an acidic amorphous alumina or molecular sieve, and isomerised hydrocarbons prepared by the process.		

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS FOR THE ISOMERISATION OF A
HYDROCARBONACEOUS FEEDSTOCK

5 The present invention relates to a process for upgrading hydrocarbonaceous feedstocks more particularly for isomerisation of a feedstock substantially boiling in the gasoline range which feedstock comprises linear paraffins having at least five carbon atoms.

10 An increasing demand placed on oil refiners is the production of gasolines meeting environmental requirements and having high octane numbers. The requirement to reduce the content of aromatics, in particular benzene, and of olefins, to reduce gasoline vapour pressure and to dispense with lead-containing additives has made necessary the identification and production of alternative high octane gasoline components. Such components, for example branched
15 gasoline range paraffins, are not typically available from main refining processes and must be obtained by upgrading of refinery fractions and added to the gasoline pool. It is an object of the present invention to provide a process for the production of such branched paraffins.

20 Processes are known for isomerisation of linear C₄-C₁₀ paraffinic feeds by contacting with certain zeolitic or amorphous catalysts in the presence of hydrogen. It has been found that bifunctional catalysts comprising certain hydrogenating-dehydrogenating metals supported on
25 a zeolite or amorphous metal oxide, such as commercially available platinum supported on mordenite (MOR) and platinum supported on chlorided alumina, give both good selectivity of reaction and improvement in stability of performance and catalyst life resulting from the presence
30 of the hydrogenating-dehydrogenating metal.

- 2 -

Moreover in European Patent no 0 398 416 is disclosed a similar process comprising contacting a similar feedstock with a catalyst comprising zeolite beta (BEA) and a hydrogenating-dehydrogenating metal or a compound thereof, the BEA having been treated with a solution having a pH of at least 9 and thereafter calcined, the metal being suitably selected from Group VIII of the Periodic Table of the Elements.

These processes give attractive yields of the desired product, notably in the upgrading of C₅-C₆ paraffinic feeds, with some yield loss incurred as a result of paraffin hydrogenolysis and cracking. In view of the fact that these processes are sensitive to catalyst deactivation as a result of poisoning by sulphur contaminants contained in the feed, it is common practice to operate feed pretreatment for removal or conversion of sulphur for example by adsorption or hydrotreatment, prior to carrying out the upgrading reaction.

It has now surprisingly been found that still further improvement in product yields and selectivities can be obtained with a process employing a catalyst comprising a specific bimetallic hydrogenation-dehydrogenation function. Moreover it would appear that these catalysts display reduced hydrogenolysis activity and increased sulphur tolerance, thereby reducing feed pretreatment duty.

Accordingly the present invention relates to a process for isomerization of a hydrocarbonaceous feedstock substantially boiling in the gasoline range which feedstock comprises linear paraffins having at least five carbon atoms wherein the feedstock is contacted in the presence of hydrogen at elevated temperature and pressure with a catalyst comprising in combination platinum and palladium each in metallic form supported on an acidic amorphous alumina or molecular

- 3 -

sieve.

Reference herein to "metallic form" is to the zero valent state of substantially all of both platinum (Pt) and palladium (Pd) present on the catalyst. It is to be appreciated that the catalyst may be employed without prior reduction of the metal components to the metallic state, whereby reduction is achieved in situ under the prevailing conditions including the presence of hydrogen.

Accordingly reference herein to "metallic form" is to the form effective during the contacting.

Reference herein to "molecular sieve" is to both zeolitic and non-zeolitic types, i.e. to molecular sieves comprised of silicoaluminate or otherwise. Preferred molecular sieves are of the "10 ring" or "12 ring" type, i.e. comprise 10 or 12 membered rings of oxygen atoms.

It is of particular advantage that the process of the present invention may be employed in the upgrading by means of isomerisation of a feed comprising paraffins of varying carbon number, for example having carbon number 5 up to 8, in a single stage. This is of particular advantage since the conversion of C₇+ component of a hydrocarbonaceous feedstock introduces problem of cracking to undesired products which problem is less prevalent with the conversion of the C₅-C₆ component. Addressing this problem by operating the process with a reduced acidity catalyst is not attractive since this of course leads to reduced conversion and the need for enhanced recycle of unreacted feedstock. Remaining options for addressing this problem include operation in two stages with use in each stage of a catalyst selective for the conversion of each component. It has now moreover been found that the process of the invention enables the isomerisation of normal paraffins to multibranched paraffins in significant yield in a single stage.

Alternatively the process of the invention enables

operation with lower total metal loading than in conventional processes without incurring yield and selectivity loss. These advantages would of course contribute to the economics of a commercial process. It has been found that the influence of Pt and Pd in combination on catalyst selectivity is greater than the sum influence of both components individually. The indication is therefore that in the process employing the bimetallic catalyst, a certain synergy in selectivity takes place.

Suitably the Pt and Pd are uniformly dispersed throughout the catalyst thereby enhancing their cooperative effect. Without being limited to the following theory, it is thought that the presence of one or both metals has an effect on the other metal, in particular the presence of the Pd seems to have a positive effect on the dispersion or the state of the Pt, whereby the metals are better brought into or retained in the metallic form. Preferably in a process employing fixed bed or other operation, the Pt and Pd are both present in the same catalyst locus, more preferably on the same catalyst particle, most preferably on the same particle of amorphous alumina or molecular sieve.

The catalyst to be used in accordance with the present invention may comprise in addition to the amorphous alumina or molecular sieve (hereinafter the active catalyst structure), a binder material comprising one or more refractory oxides.

The Pt and Pd metals may be present on the active catalyst structure or may be present on a separate carrier (e.g. the binder) comprising for instance one or more refractory oxides, e.g. alumina. Preferably the Pt and Pd are present on the active catalyst structure.

Suitably the Pt and Pd are loaded onto the active catalyst structure by methods known in the art, for

- 5 -

example by means of (competitive) ion-exchange,
(competitive) pore volume (incipient wetness)
impregnation, controlled deposition precipitation,
comulling in a suitable mixing device a precursor of the
5 metallic components onto the active catalyst structure
and/or binder. Preferably the metals are loaded onto the
active catalyst structure by means of incipient wetness
impregnation of an aqueous solution of the tetramine-
dichloride salt, or by means of competitive ion exchange
10 in the presence of ammonium as competitive ion.

In a further advantage, the process of the invention
is substantially independent of the manner in which the
metals are loaded onto the catalyst. This is in contrast
to processes using catalysts comprising only Pt or only
15 Pd, whereby process performance can be affected by manner
of loading of metal onto the active catalyst structure.

In particular, known processes employing catalysts
prepared by competitive ion exchange of only Pt or only
Pd display stable, high performance operation over a
20 typical temperature range, which we believe is the result
of improved metal dispersion and reduced excess acidity,
and with respect to the platinum component, reduced
hydrogenolysis activity.

It is found that the present process advantageously
25 provides improved catalyst performance which would seem
to override any improvement available by manner of
catalyst synthesis. Without being limited to the
following theory, it is thought that the catalysts
employed in the process of the present invention are
30 characterized by improved metal dispersion and reduction
to the metallic state when compared with the known
monometallic catalysts.

Suitably the metals are introduced simultaneously.
Suitably the metals are distributed in the active
35 catalyst structure. Suitably distribution is controlled

- 6 -

by means of control of solution composition during introduction, for example by control of solution pH and competitive anions and cations content. Suitably the metals are brought into metallic form by reduction procedures known in the art. Suitably the catalyst comprises from 0.01 to 5% by weight of Pt and Pd in combination based on total weight of active catalyst structure, preferably from 0.1 to 3% by weight of combined Pt and Pd based on total weight of active catalyst structure. Suitably the Pt and Pd are present in an atomic ratio of Pt/(Pt + Pd) of between 0.0 and 1.0, preferably of substantially 0.1 to 0.8, more preferably of substantially 0.1 to 0.5.

Amorphous alumina catalysts which may be employed in the process of the present invention include those known in the art. Suitably amorphous alumina catalysts are characterised by moderate to low surface area, preferably surface area of 100-500 m²/g. More preferably amorphous alumina catalysts comprise eta alumina or gamma alumina, of 320-430 m²/g or 170-220 m²/g respectively.

The amorphous alumina may comprise an additional acidic component. Suitably amorphous alumina catalysts comprise a chloride component whereby acidity is enhanced. Suitably amorphous alumina catalysts are chlorided by known means including subliming AlCl₃ and reaction with COCl₂, CCl₄ etc. Suitably acidic components are present at a level suitable to achieve the desired acidity. In particular eta alumina may comprise chlorine in amount of 5-15%, gamma alumina in an amount of 3-8%.

Molecular sieves which may be employed in the present invention include any zeolitic or non-zeolitic molecular sieves capable of selective conversion of feed molecules in the range above defined. Typically such molecular sieves are, but are not limited to, those typically known as medium pore type natural or synthetic molecular

- 7 -

sieves. Preferred zeolites are of the "10 ring" or "12 ring" type, i.e. comprise 10 or 12 membered rings of oxygen atoms, and are preferably of the twelve ring type including as non-limiting example MCM-22 and AEL, AFI, AFR, AFS, AFY, ATO, ATS, BEA, BOG, BPH, CAV, EHT, FAU, GME, LTL, MAZ, MEI, MOR, MTW and OFF as described in "Zeolites" Vol. 12 No. 5 (1992), with the exception of MCM-22 which is described in US Patent 4,954,325. More preferred are AEL, BEA, FAU, MOR, MTW and OFF.

Non-zeolitic molecular sieves given as non-limiting example, in particular AEL, AFI, AFR, AFS, AFY, ATD and ATS, which include a metal component, suitably include a Group VIII metal component, preferably selected from magnesium, manganese, cobalt and zinc, more preferably cobalt.

Molecular sieves of the zeolite or non-zeolite type may be selected or modified to obtain a desired level of acidity. Zeolites may be conveniently modified or synthesised in manner to attain a given ratio of SiO_2 to Al_2O_3 , whereby the acidity is determined. Suitable ratios of SiO_2 to Al_2O_3 are dependent on the individual zeolite to be employed. Typically for example a zeolite of the MOR type may be employed with a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 10 to 60, preferably 15 to 30, for example of approximately 20. The zeolite may further be modified to optimise selectivity for example by treatment of non-selective acidic sites, typically non pore-internal acid sites, which treatment or modification is well known, and may comprise acid or base treatment or modification.

Suitably the process is carried out at a temperature of 50 to 400 °C, a pressure of up to 5×10^6 Pa (50 bar), a space velocity of 0.5 to 10 kg/kg.h and a hydrogen to feedstock molar ratio of up to 10.0.

When use is made of an amorphous alumina catalyst the process is suitably carried out at a temperature of from

- 8 -

5 50 to 250 °C, preferably of from 100 to 150 °C, a total pressure of 1.5×10^6 to 4×10^6 Pa (15 to 40 bar), preferably of 3×10^6 Pa (30 bar), a space velocity of 0.3 to 10 kg/kg.hr, preferably of 0.5 to 5 kg/kg.hr and a hydrogen to feedstock molar ratio of up to 10.0, preferably of from 0.01 to 3.0.

10 When use is made of a zeolite molecular sieve catalyst, the process is suitably carried out at a temperature of from 150 to 350 °C, preferably of from 180 to 280 °C, a total pressure of 1.5×10^6 to 3.5×10^6 Pa (15 to 35 bar), for example approximately 2.5×10^6 Pa (25 bar), a space velocity of 0.5 to 5 kg/kg.hr and a hydrogen to feedstock molar ratio of up to 5.0, preferably of from 0.5 to 4.0.

15 When use is made of a non-zeolite molecular sieve catalyst, the process is suitably carried out at a temperature of from 250 to 450 °C, preferably of from 275 to 400 °C, a total pressure of up to 1×10^7 Pa (100 bar), preferably of from 1×10^6 to 5×10^6 Pa (10 to 50 bar), a space velocity of from 0.5 to 10.0 kg/kg.h, preferably of from 1.0 to 5.0 kg/kg.h and a hydrogen to feedstock molar ratio of up to 5.0, preferably of from 1.0 to 3.0.

25 The hydrocarbonaceous feedstock substantially boiling in the gasoline range can suitably be obtained by fractionating any paraffinic gasoline-containing hydrocarbonaceous feedstock.

30 Preferably the feedstock substantially boiling in the gasoline range is obtained by subjecting a straight run hydrocarbon oil to a fractionation, preferably atmospheric distillation. Other suitable hydrocarbonaceous feedstocks substantially boiling in the gasoline range include product fractions obtained from cracking processes such as catalytic cracking, thermal cracking, delayed coking, visbreaking and flexicoking.

35

- 9 -

Hydrocarbonaceous feedstocks containing unacceptable levels of sulphur and nitrogen may be subjected to a hydrotreatment before they are subjected to the process according to the present invention, whereby particularly advantageous results may be obtained. Suitably the hydrocarbonaceous feedstock boiling in the gasoline range has a low sulphur content, preferably less than 10 ppmw on feed.

The hydrocarbonaceous feedstock may consist entirely of a fraction boiling in the gasoline range, i.e. in the range of C₄-220 °C. While the full gasoline boiling range fraction may be included in the hydrocarbonaceous feedstock, it may be preferred to employ as hydrocarbonaceous feedstock a cut thereof having a boiling point up to 180 °C. Optionally, the hydrocarbonaceous feedstock may be blended with a reformat fraction.

Suitably, the hydrocarbonaceous feedstock substantially boiling in the gasoline range may substantially comprise linear paraffins having at least five carbon atoms, i.e. the feedstock may substantially consist of one or more different types of linear paraffins having at least five carbon atoms.

Preferably, the hydrocarbonaceous feedstock boiling in the gasoline range substantially comprises linear paraffins having five to ten carbon atoms. More preferably, the hydrocarbonaceous feedstock substantially comprises linear paraffins having five to seven carbon atoms. Suitably, the hydrocarbonaceous feedstock substantially comprises n-hexane and/or n-heptane.

In a further advantage the process of the present invention is characterised by an enhanced performance in the conversion of sulphur contaminated feedstocks, by virtue of the enhanced total activity observed. Moreover it would seem that the process is characterised by an

- 10 -

enhanced resilience to the poisoning effect of sulphur contaminants present in feedstocks to be converted. It is of particular advantage to process a refinery feedstock without the need for a preliminary feed purification step, or with the possibility to reduce the duty of feed pretreatment.

Accordingly the present invention relates in a further embodiment to a process for isomerisation of a hydrocarbonaceous feedstock substantially boiling in the gasoline range which feedstock comprises linear paraffins having at least five carbon atoms and has a sulphur content of greater than or equal to 10 ppm wherein the feedstock is contacted in the presence of hydrogen at elevated temperature and pressure with a catalyst comprising in combination Pt and Pd each in metallic form supported on an acidic amorphous alumina or molecular sieve.

Suitably the process comprises isomerization of a feedstock as above defined having a sulphur content in the range of 10 to 100 ppm, preferably 10 to 50 ppm, more preferably 10 to 30 ppm, for example approximately 20 ppm. Suitably operation with higher sulphur content feeds is performed at slightly higher severity, for example at temperatures slightly greater than required with conversion of low sulphur content feedstocks.

Suitably unconverted linear paraffins are separated from branched paraffins downstream of the reaction zone in which the isomerisation is carried out, and recycled to the reaction zone. Separation can suitably be carried out by means of molecular sieve or of distillation.

The process is suitably initiated by loading the reaction vessel with catalyst and heating the bed with simultaneous activation of the catalyst by contacting with flowing oxygen at elevated temperature and subsequently with flowing hydrogen at elevated

- 11 -

temperature. The feedstock to be isomerised is suitably preheated to elevated temperature which may be less than or equal to the operating temperature and is introduced at a desired rate together with hydrogen in desired molar ratio.

The reaction is suitably terminated on partial or complete deactivation of the catalyst, and catalyst regeneration performed. Regeneration may be performed after terminating the feedstock supply, by introducing a suitable regeneration medium or by raising the catalyst to elevated temperature for combustion of deactivating hydrocarbonaceous deposits. Suitable regeneration media include reactive or adsorptive fluids as known in the art, for example a combustion gas such as diluted air or oxygen/nitrogen mixtures.

The process may be carried out in any desired reactor, and is suitably carried out in a fixed bed, slurry or fluidised bed reactor, in batch, semi-continuous or continuous mode. A plurality of reactors may be employed in series or parallel. Regeneration of the catalyst may be carried out in one or more reactors simultaneously with operation of the process in one or more of the remaining reactors.

In a further aspect the present invention relates to isomerised paraffinic hydrocarbons whenever prepared by a process as hereinbefore described.

The invention will now be illustrated in non-limiting manner by means of the following examples.

Example 1 - Preparation of bifunctional bimetallic Catalysts A

Samples of BEA zeolite of Si to Al atomic ratio of 12.5, surface area of 750 m²/g and crystal size of 0.1 to 0.7 micron were converted to the ammonium form by contacting the sample with an aqueous solution of ammonium chloride at a pH of 8. Platinum (Pt) and

- 12 -

palladium (Pd) were then introduced onto the samples in desired amounts by contacting the samples with a Pt/Pd tetramine dichloride solution, by known technique of competitive ion exchange in the presence of ammonium as competitive ion. The samples thus obtained were activated in situ by calcination in flowing oxygen (15 mol/kg.s) at 400 °C, followed by reduction in flowing hydrogen (15 mol/kg.s) at 400 °C. Catalysts A were thus obtained having both Pt and Pd present in independently varied amounts, expressed as ratio $Pt/(Pt + Pd)$ of between 0.0 and 1.0. Total metal loading (Pt + Pd) included 0.5 wt%, 1.0 wt% and 1.5 wt% on weight of active catalyst structure for different samples.

Example 2 (Comparative) - Preparation of bifunctional monometallic Catalysts B and C

Catalysts B and C were prepared following the same procedure as given in Example 1 above, with the exception that for each sample of ammonium form BEA zeolite only one of platinum and palladium metal was introduced. Catalysts B were obtained having only Pt present in varied amounts equal to the total metal loading of Catalysts A, and Catalysts C were obtained having only Pd present in varied amounts equal to the total metal loading of Catalysts A, expressed as ratio $Pt/(Pt + Pd)$ of 1.0 and of 0.0 respectively.

Example 3 - Isomerisation of n-heptane feedstock

Heptane conversion was carried out in a fully automated continuous flow tubular microreactor. A sample of Catalyst A, B, C or mixture of B and C prepared in Example 1 or 2 above was activated in situ in the reactor as above described. A stream of hydrogen saturated with heptane vapour was then generated using a thermostatted saturator. The purity of heptane was at least 99%, with 1% or less impurities comprised mainly of isomers of heptane. Reaction products were analysed on line by gas

- 13 -

5 chromatography. Conversion was maintained at 82.5%, by means of adjusting the space velocity. Conversion was carried out at 220 °C, a hydrogen to heptane molar ratio of 60 and a total pressure of 0.3 MPa (3 bar). Product obtained comprised a mixture of cracked hydrocarbons having less than 7 carbon atoms, and of isomerised hydrocarbons having 7 carbon atoms. The results are given in Tables 1 to 3 below.

10 TABLE 1 - Isomer Yield (%) as a function of Pt/(Pt + Pd) ratio for isomerisation of heptane over Catalysts A, B, C, B and C.

CATALYST A,B,C,B + C Pt/(Pt + Pd)	ISOMER YIELD (%)		
	(Pt + Pd) = 0.5 wt%	(Pt + Pd) = 1.0 wt%	(Pt + Pd) = 1.5 wt%
C 0.00	73.0		
A 0.23	75.0 (72.1)		
A 0.50	74.6 (71.0)		
A 0.69	73.3 (70.3)		
B 1.00	69.1		
C 0.00		73.4	
A 0.35		74.8 (70.5)	
A 0.85		71.7 (69.3)	
B 1.00		65.0	
C 0.00 + B 1.00	< 60.0		
A 0.33			74.0

15 In the table, values in brackets correspond to the calculated value which would be expected with a bimetallic catalyst having performance equal to the additive performance of the individual metal components, this value is calculated as a simple additive function.

From the table it is apparent that the isomer yields

- 14 -

5 of Catalysts A comprising both Pt and Pd in combination exceed the calculated sum isomer yields of Catalysts B and C, and significantly exceed the measured sum isomer yield (physical mixture Catalysts B + C). This is seen to be reproducible for different absolute metal loadings, with preference for catalysts having Pt/(Pt + Pd) of 0.1 to 0.5.

TABLE 2 - Yield of monobranched and multibranched isomers (%) as a function of Pt/(Pt + Pd) ratio for isomerisation of heptane over Catalysts A, B and C.

CATALYST A,B,C Pt/(Pt + Pd)	MONOBRANCHED (%)			MULTIBRANCHED (%)		
	(Pt + Pd) = 0.5 wt%	(Pt + Pd) = 1.0 wt%	(Pt + Pd) = 1.5 wt%	(Pt + Pd) = 0.5 wt%	(Pt + Pd) = 1.0 wt%	(Pt + Pd) = 1.5 wt%
0.00 (C)	51.5			21.6		
0.23 (A)	51.6 (51.0)			23.4 (21.2)		
0.50 (A)	53.6 (50.4)			21.0 (20.7)		
0.69 (A)	52.7 (50.0)			20.6 (20.4)		
1.00 (B)	49.3			19.8		
0.00 (C)		51.2			22.2	
0.35 (A)		50.9 (50.3)			23.9 (22.1)	
0.85 (A)		49.8 (49.1)			21.9 (21.9)	
1.00 (B)		46.4			18.6	
0.33 (A)			52.4			21.6

5 In the table, values in brackets correspond to the calculated value which would be expected with a bimetallic catalyst having performance equal to the additive performance of the individual metal components. This value is calculated as a simple additive function.

10 From the Table it is apparent that the yields of mono and of multibranched isomers obtained with Catalysts A exceed the sum monobranched isomer and sum multibranched isomer yields of the process using Catalysts B and C. Moreover for Catalysts A wherein $Pt/(Pt + Pd)$ is 0.1 to 0.5, enhancement of isomer yield comprising predominantly multibranched isomers is obtained in a single step according to the process of the invention.

15 TABLE 3 - Product Yield breakdown of process Example 3

Total product breakdown is given in the following Table, for the process using Catalyst A, $Pt/(Pt + Pd) = 0.23$, $Pt + Pd = 0.5$ wt% and for the process using Catalyst C, $Pd = 0.5$ wt%, and using Catalyst B, $Pt = 0.5$ wt%.

- 17 -

Product	Octane Rating (RON)	Yield (mol %)			Product	Yield (mol %)		
		A	C	B		A	C	B
n C ₇	0	17.5	17.5	17.5	C ₁	0.0	0	0.3
2-MeC ₆	42.4	24.8	25.1	24.0	C ₂	0.0	0	0.4
3-MeC ₆	52.0	25.1	24.6	23.6	C ₃	3.7	4.6	5.8
3-EtC ₅	65.0	1.7	1.8	1.7	nC ₄	0.0	0.1	1.4
2,2-	92.8	6.7	6.1	5.3	iC ₄	3.8	4.8	4.5
diMeC ₅								
2,4-	83.1	5.8	6.0	5.7	C ₅	0.0	0	0.4
diMeC ₅								
3,3-		3.0	2.5	2.0	C ₆	0.0	0	0.5
diMeC ₅								
2,3-	91.1	7.7	6.6	6.6				
diMeC ₅								
2,2,3-	>100	0.3	0.4	0.3				
triMeC ₄								

From the above Table it is clear that improved quality of product is obtained by the process of the present invention, with substantially no cracking of feed molecules taking place, and with attractive yields of high octane rating multibranched components. Octane ratings are obtained from "Automotive Fuels Handbook" K. Owen, T. Coley, SAE International 1990 p. 564 (ISBN 1-56091-064-x). For other Catalysts A, with total metal loadings up to 1.5 wt%, product quality was almost identical. In comparison, the product yields obtained with the Catalyst B and C show a substantial amount of cracked C₃ and C₄ product and less attractive yields of high octane rating components.

C L A I M S

1. Process for isomerisation of a hydrocarbonaceous feedstock substantially boiling in the gasoline range which feedstock comprises linear paraffins having at least five carbon atoms wherein the feedstock is contacted in the presence of hydrogen at elevated temperature and pressure with a catalyst comprising in combination platinum (Pt) and palladium (Pd) each in metallic form supported on an acidic amorphous alumina or molecular sieve.
2. Process according to claim 1 wherein the Pt and Pd are both present on the same locus, more preferably on the same catalyst particle, most preferably on the same particle of amorphous alumina or molecular sieve.
3. Process according to claim 1 or 2 wherein the catalyst comprises from 0.01 to 5% by weight of Pt and Pd in combination based on total weight of active catalyst structure, preferably from 0.1 to 3% by weight thereof.
4. Process according to any of claims 1 to 3 wherein Pt and Pd are present in an atomic ratio of Pt/(Pt + Pd) of between 0.0 and 1.0, preferably of substantially 0.1 to 0.8, more preferably of substantially 0.1 to 0.5.
5. Process according to any of claims 1 to 4 wherein an amorphous alumina catalyst comprises a moderate to low surface area, preferably surface area of 100-500 m²/g.
6. Process according to any of claims 1 to 5 wherein the amorphous alumina comprises an additional acidic component.
7. Process according to any of claims 1 to 6 wherein acidic molecular sieve is of the "twelve ring type" as hereinbefore defined, including for example MCM-22 and AEL, AFI, AFR, AFS, AFY, ATO, ATS, BEA, BOG, BPH, CAV,

EHT, FAU, GME, LTL, MAZ, MEI, MOR, MTW and OFF as hereinbefore defined.

5 8. Process according to any of claims 1 to 7 which is carried out at a temperature of 50 to 400 °C, a pressure of up to 5×10^6 Pa (50 bar), a space velocity of 0.5 to 10 kg/kg.h and a hydrogen to feedstock molar ratio of up to 10.0.

10 9. Process according to any of claims 1 to 8 wherein the feedstock is obtained by fractionating any paraffinic gasoline-containing hydrocarbonaceous feedstock, preferably by subjecting a straight run hydrocarbon oil to fractionation, more preferably atmospheric distillation.

15 10. Process according to any of claims 1 to 9 wherein the feedstock substantially comprises linear paraffins having five to ten carbon atoms.

20 11. Process according to any of claims 1 to 10 wherein the feedstock has a sulphur content of greater than or equal to 10 ppm, suitably in the range of 10 to 100 ppm, preferably 10 to 50 ppm, more preferably 10 to 30 ppm, for example approximately 20 ppm.

25 12. Process according to claim 11 wherein unconverted linear paraffins are separated from branched paraffins downstream of the reaction zone in which the isomerisation is carried out, and recycled to the reaction zone.

13. Isomerised paraffinic hydrocarbons whenever prepared by a process according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/04997

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G45/62 C07C5/27

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10G C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 925 503 (W.R. GRACE & CO) 9 December 1975 see claims 1-3 see column 1, line 46 - line 57 ---	1,3,4, 8-10
A	EP,A,0 398 416 (SHELL) 22 November 1990 cited in the application see claims 1,6,8,9 see page 3, line 7 - line 27 ---	1,8-10, 12,13
A	US,A,4 489 216 (TEXACO) 18 December 1984 see claims 1-5 see page 4, line 56 - line 64 see page 5, line 4 - line 12 ---	1,8-10
A	US,A,4 992 402 (EXXON) 12 February 1991 see claims 1-3 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

22 March 1996

Date of mailing of the international search report

04 -04- 1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

De Herdt, O

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/04997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3925503	09-12-75	CA-A- 1058227	10-07-79
EP-A-398416	22-11-90	AU-B- 620514	20-02-92
		AU-B- 5496590	15-11-90
		DE-D- 69022879	16-11-95
		DE-T- 69022879	21-03-96
		JP-A- 3020228	29-01-91
		US-A- 5055629	08-10-91
US-A-4489216	18-12-84	US-A- 4716137	29-12-87
US-A-4992402	12-02-91	NONE	

THIS PAGE BLANK COPY
BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)